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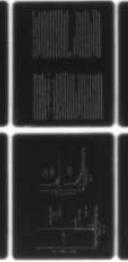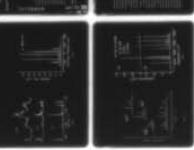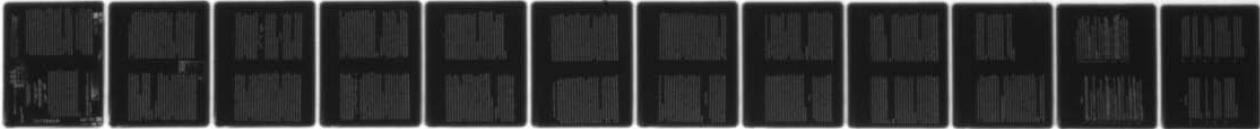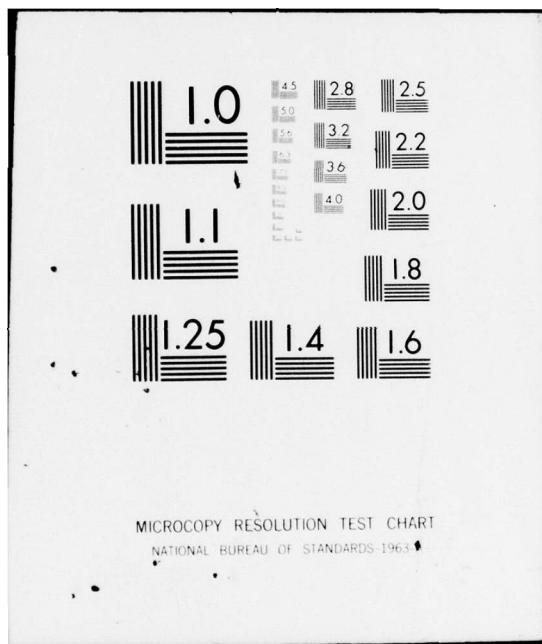
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MOLECULAR OPTICAL SPECTROSCOPY WITH
SUPERSONIC BEAMS AND JETS

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This account is a description of a recent technique which is directed toward over-coming two difficulties which arise when one wishes to study the high resolution spectra of molecules. The first of these is the necessity of obtaining a sample of the molecules at a temperature which is low enough to prevent thermal dissociation and which contains a population of only as many rotational and vibrational levels of the molecular system as can be separately assigned in the spectrum. The second difficulty lies in finding a medium which will support the molecular system at this low temperature without introducing un-desirable changes and complications in the spectrum. A desirable spectroscopic sample would be an ensemble of molecules, all in a particular and well-defined quantum state (usually the lowest energy allowed state) traveling in free space with a narrow velocity distribution, and at a sufficiently low density so that intermolecular interactions are unim-portant.

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A supersonic expansion of molecules in an inert, monatomic carrier gas seems, to a large degree, to satisfy the requirements of an ideal spectroscopic sample. In the course of such a supersonic expansion, the translational temperature of the carrier gas falls to an extremely low value – less than 0.03K in some cases. Polyatomic molecules seeded into this expanding gas communicate with the low temperature bath provided by the monatomic carrier via two-body collisions, causing the translational and rotational degrees of free-dom of the molecules to cool to comparably low temperatures. Vibrational cooling, although less complete than rotational cooling, can also be quite extensive. The rapidly falling temperature and density in the resultant supersonic jet quickly brings the expanding gas into a condition of free, collisionless flow, permitting molecular species which would otherwise be highly unstable to survive, unperturbed, at a very low temperature for a period of time limited only by the size of the apparatus. Because this cooling occurs so quickly, in a manner which minimizes three-body collisions, the cooling may be achieved without extensive condensation.

The purpose of this account is to trace the progress of research in the application of supersonic beams and jets toward the solution of a number of problems in molecular optical spectroscopy and to illustrate the promise such experiments hold for future work.

COOLING IN SUPERSONIC BEAMS AND JETS: ATOMIC GASES

Atomic gases are preferable to molecular gases in obtaining the lowest temperatures because they do not store energy in rotational and vibrational degrees of freedom. Hence, for a given expansion ratio they will achieve a lower temperature. A free jet of pure helium has been shown capable of cooling to $0.03K^1$ through expansion into vacuum from room temperature and about 100 atm, and a pure argon jet can be cooled to 2K or so.^{2}

Both gases as well as mixtures of them have been used as refrigerants and reactants in the work to be discussed. Helium has the additional advantage of forming no stable He_2 complex in the ground electronic state, and is therefore capable of sustaining a greater upstream density without forming polymers downstream. As a practical matter this allows lower ultimate temperatures for helium expansions.

The percentage of added molecule is generally so small that the conditions achieved in the expanding carried gas can be understood in terms of the behavior of the free expansion of the pure gas, and we therefore first discuss the properties of a supersonic expansion of a monatomic gas.

A. Expansion of a Monatomic Gas

A molecular beam source consists of a high pressure gas reservoir, an orifice in the reservoir to allow the escape of gas, various collimating apertures to shape the downstream flow pattern in some desired manner, and adequate pumping capacity to maintain low downstream pressure. If the collimating apertures are absent and there is no attempt to control the downstream flow pattern, a supersonic source is called a free jet.

The earliest and still the most familiar molecular beams are the effusive beams[3] in which the orifice size is so small that $D << \lambda_0$, where D is some characteristic orifice dimension (the diameter in the case of a circular orifice), and λ_0 is the mean free path of the gas at pressure P_0, the pressure inside the reservoir. In an effusive source, the flow from the orifice is molecular since there are substantially no collisions between gas molecules downstream of the orifice, and the velocity distribution in the beam is the velocity weighted Boltzmann distribution characteristic of the reservoir temperature. More important from the point of view of the spectroscopist, the distribution of internal molecular states is identical to that in the reservoir. Although the effusive beam offers

many advantages to the spectroscopist, cooling is not one of them.

In 1958, Kantrowitz and Grey[4] proposed the supersonic jet as a molecular beam source. Although their motivation seems to have been primarily an improvement in beam intensity, they were fully aware that their suggested source would also produce a cooling of the translational and internal degrees of freedom of the molecules in the beam. In the jet, the reservoir pressure or the orifice size is increased to the point where $D >> \lambda_0$. There will be many collisions as the gas flows through the orifice and downstream of the orifice, and such a flow regime is termed hydrodynamic. The hydrodynamic expansion converts the enthalpy associated with random atomic motion into directed mass flow,[5] and this process therefore causes the mass flow velocity, u, to increase. The conversion of random motion to directed mass flow causes the temperature to decrease, and since the classical speed of sound, a, is defined as $\sqrt{\gamma k T/m}$, the speed of sound decreases and the Mach number, $M \equiv u/a$, increases. In the ideal expansion $M = 1$ at the most constricted point of the nozzle, and with additional expansion $M > 1$, and the flow is termed supersonic, hence the title of this article. Kantrowitz and Grey emphasized the use of a skimmer to maintain adequately low downstream pressures, but a skimmer is not used in the technique we describe here.

It is instructive to discuss the meaning of translational temperature in such a flow regime. In an effusive beam the velocity distribution is given by the velocity-weighted Maxwell-Boltzmann distribution shown by the dashed curve in Fig. 1. This distribution has a peak at $v = \sqrt{3kT/m}$ and a standard deviation in velocity $= \sqrt{0.47\ kT/m}$. A gas that has expanded through a supersonic nozzle, has a velocity distribution in the direction of mass flow illustrated by the solid curve in Fig. 1. Because of the increase in flow velocity, the peak of the distribution has shifted to higher velocity and because the gas
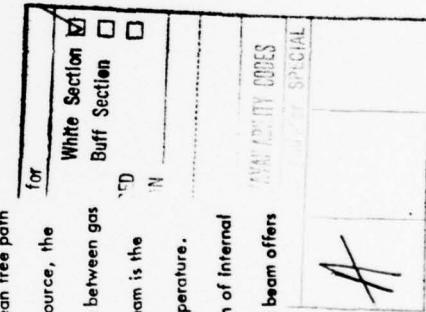
has cooled, the distribution narrows. The translational temperature is determined by the width of the velocity distribution and not by the position of the peak. From the point of view of an observer moving downstream at the flow velocity u, the relative velocity between him and the gas determines the temperature he experiences. The flow velocity of the whole mass of gas is irrelevant (until it hits a wall).

As described above, the primary process in the supersonic expansion is a cooling of the translational degrees of freedom. The actual state of the beam depends on the rate at which the other degrees of freedom come into equilibrium with the cold translational bath. The utility of supersonic beams for spectroscopic applications lies in the fact that the equilibration rates are very different for the different degrees of freedom, and therefore there is the possibility of producing at some point in the expansion a highly nonequilibrium state. Eventually the expansion proceeds to the point where the density is so low that there are no further collisions, and from this point on the distributions of the various degrees of freedom are frozen in and do not change. If the beam is in a nonequilibrium state when it enters the collision free region, it stays that way for some appreciable time until it encounters an obstacle (such as the walls of the apparatus). During this time one may perform experiments which take advantage of the nonequilibrium distribution.

It is generally true that the rate of equilibration between translations and rotations is relatively fast, and therefore extensive rotational cooling takes place before the molecules enter the collision free region. The rate of vibration-translation equilibration of a particular vibrational mode is generally slower. Therefore the vibrational cooling is not nearly as complete as rotational cooling but, as we will later demonstrate, some vibrational cooling does occur. Most significantly, the rate of phase equilibration is very slow and the molecules persist for a long time in the gas phase at temperatures far lower than that necessary

to freeze the entire system into a solid. The result is that when the molecules enter the collision free region the system can be translationally and rotationally very cold, vibrationally somewhat cold, but still consisting of single isolated gas phase molecules.

It now seems reasonable to ask: how cold can the jet become? Under adiabatic reversible flow conditions (no shock waves, no shear forces, no heat sources or sinks, and no heat conductivity) the expansion is isentropic and one may use the isentropic equation of state of an ideal gas to describe the temperature, pressure, and density of the beam as a function of the extent of the expansion. These assumptions give the result:[6]

$$\frac{T}{T_0} = \frac{P}{P_0}^{(\gamma-1)/\gamma} = \frac{\rho}{\rho_0}^{\gamma-1} = \frac{1}{1+\frac{1}{2}(\gamma-1)M^2} \qquad (1)$$

where T_0, P_0, and ρ_0 are the temperature, pressure, and density in the reservoir; T, P, and ρ are the same quantities in the beam; γ is the heat capacity ratio C_p/C_v; and M is the Mach number. If the expanding gas is treated as a continuous medium, the method of characteristics[7] may be used to determine the Mach number as a function of distance downstream of the nozzle and this result is

$$M = A(X/D)^{\gamma-1} \qquad (2)$$

where X is the distance from the nozzle, D is the nozzle diameter, and A is a constant which depends on γ and is equal to 3.26 for a monatomic gas. Thus as one examines the conditions downstream of the orifice, the Mach number increases and the temperature, pressure, and density all decrease.

As Anderson and Fenn[8] have shown, this process cannot go on forever. Equation (2) was derived on the assumption that the gas was continuous, whereas in reality it is made up of discrete atoms and molecules. Eventually the density drops to the point where the

two-body collision rate cannot sustain the redistribution of velocity required by the hydro-
dynamic equations of flow. The total number of collisions possible is finite, and hence
the Mach number, and also the temperature, asymptotically approach terminal values.
Anderson and Fenn's model for this process of Mach number freezing treats the particles as
classical hard spheres and concludes that the terminal Mach number is given by

$$M_T = 2.05 \, \epsilon^{-(1-\gamma/\gamma)} (\Lambda_0/D)^{(1-\gamma)/\gamma} = 133(P_0 D)^{0.4} \text{ (for argon)} \quad (3)$$

where ϵ is the collisional effectiveness constant of Oman et al[9] relating the
change in mean random velocity per collision to the present mean random velocity. The
quantity $2.05(\epsilon)^{(\gamma-1)/\gamma}$ reduces to the value 133 for argon when the reservoir pressure
is in atmospheres and the nozzle diameter is in cm. Recent work by Toennies et al[10] has
indicated that for helium at low temperature, quantum effects and the variation of the inter-
molecular potential with distance cause the collisional cross section to rapidly increase
with decreasing translational energy of the colliding pair. The result of this quantum
effect is to cause the terminal Mach number to increase more rapidly with $P_0 D$ than indi-
cated by Eq. (3). This effect is illustrated in Fig. 2.

The mention of high Mach numbers suggests that the gas is moving at a very high
velocity, but this is not the case. As we have seen, the isentropic expansion converts
random thermal motion into directed mass flow. Since there is only a finite amount of
random energy, the increase in mass flow velocity must be finite even in the case of
infinite Mach number where all of the random energy is converted. In fact, at infinite
Mach number the mass flow velocity is only $\sqrt{5/3} = 1.29$ times as large as the most
probable speed of molecules in an effusive beam. This limiting value is approached
early on in the expansion and from then on the mass flow velocity increases hardly at all.
Of course the temperature and the local speed of sound continue to drop and the Mach

number continues to rise. Thus the very high Mach numbers in which we will be interested
are achieved by lowering the speed of sound, not by raising the flow velocity.

One interesting consequence of this is that since the flow velocity is constant for
most of the expansion, the distance a molecule travels downstream is proportional to the
time since it left the nozzle. Equation (2) shows that as the nozzle diameter is increased,
the expansion field becomes bigger, i.e., that molecules must travel farther to attain a
given Mach number. The constant flow velocity requires that for a larger nozzle diameter,
they also travel longer to achieve a given Mach number, and that the nozzle diameter is a
measure of how long they must travel. Since the probability per unit time that a molecule
will make a binary collision is proportional to the pressure, the quantity $P_0 D$ is proportional
to the total number of binary collisions a molecule makes before it achieves a given Mach
number. Thus the fact that the terminal Mach number is a function of $P_0 D$ is simply a
statement that it is a function of the total number of binary collisions an average molecule
undergoes.

B. Condensation and Complex Formation

Complex formation sets another limit upon the degree of cooling that it is possible
to achieve. We have said that condensation is slow and this is an important reason that
supersonic beams are useful. Nevertheless, at some point atoms and molecules in the
beam will start to polymerize, and this happens as an irreversible process. The interatomic
binding energy is released and may reappear in the form of translational kinetic energy
which reheats the beam and limits the translational temperature.

One minimizes condensation of the carrier atoms by using helium which has very weak
intermolecular forces. Since there appears to be no bound He_2 molecule,[11] the formation
of pure helium clusters requires at least four body collisions for initiation, and thus the

growth of such clusters is a very slow process. As a practical matter the growth of com-
plexes of helium and the molecule of spectroscopic interest which has been seeded into the
helium beam occurs long before the formation of pure helium clusters. Of course the
formation of helium-molecule complexes can be kept from reheating the beam by keeping
the concentration of molecules low, but the growth of these complexes ultimately limits
the degree of cooling achievable in the study of the isolated molecule.

The formation of complexes requires at least three body collisions while the cooling
of the beam requires only two body collisions, and the ratio of three body collisions to two
body collisions is proportional to n_o, the number density of atoms. We have seen that the
terminal Mach number and terminal temperature are functions of $n_o D$, and therefore for a
given terminal temperature one can minimize complex formation by decreasing n_o and
increasing D, keeping $n_o D$ constant. However, since the mass throughput through the
nozzle, and ultimately through the pumps, is proportional to $n_o D^2$, the increase in nozzle
diameter increases pump size. For a given pump size one would wish to decrease n_o and
increase D to minimize complex formation. Thus high pumping speed is always advantageous,
but for a given pump, some compromise between high Mach number and low complex forma-
tion is prudent to obtain lowest temperatures.

C. Pumping Requirements

If one is to achieve low beam temperatures, one must avoid scattering the beam
molecules off of molecules of the ambient background gas since the background gas is at
room temperature, and therefore scattering would reheat the beam. The usual technique
for minimizing interaction with the background is to pump down to a low enough pressure
so that the mean free time between collisions is much larger than the transit time across
the apparatus. This usually requires a vacuum of $10^{-3} - 10^{-4}$ torr in the region between

the nozzle and the first collimating aperture (the skimmer) and a vacuum of $10^{-5} - 10^{-6}$
in the region downstream of the skimmer. In 1964 Campargue[12] proposed the substitution
of pumps capable of high mass throughput in place of pumps of high volumetric speeds in
the expansion region, and operation at higher reservoir and expansion chamber pressures.
If one allows the pressure in the expansion chamber to rise, a shock system surrounds the
jet as shown in Fig. 3. It had previously been observed[13] that background gas did not
penetrate these shock waves under higher pressures of operation and that therefore the
region inside the shock system, the isentropic core, is in a "zone of silence" which be-
haves as through the background gas were not there. Of course once molecules pass into
the shock waves, they are reheated and therefore one must either perform experiments
inside the shock structure or else extract the isentropic core into a region of high vacuum
with a very well designed skimmer.

The advantage of Campargue's technique is that the pumping of the expansion chamber
is being done at a much higher pressure. Although the mass throughput depends only on the
reservoir pressure and the nozzle diameter, the required volumetric pumping speed required
for a given mass throughput is inversely proportional to the chamber pressure. Therefore, a
pump of a given volumetric speed removes more mass when operating at a higher pressure and
therefore $P_o D$ and, hence, the terminal Mach number may be increased.

In the examples to be discussed below the expansion chamber pumps consisted of
either a liquid hydrogen cooled cryopump (for the earlier argon expansions), or one to
three booster jet diffusion pumps having a peak rated pumping speed for air of 260 l/sec
at about .03 torr.

OPTICAL SPECTROSCOPY IN SUPERSONIC BEAMS AND JETS

Although the idea that supersonic free expansions may be usefully employed in molecular physics is quite old,[14] one of the earliest detailed suggestion that these devices could be usefully employed in molecular spectroscopy was made by Milne and Greene[15] in 1969. In this article (which contains a fine review of the general utility of supersonic expansions) they introduce the concept of a "Free Jet Isolation Spectroscopy," wherein the emphasis is on "the ability of a free jet both to reduce the internal energy of its constituents and, by expansion to essentially collisionless flow, to effectively isolate them from interaction with other matter." Milne and Greene also emphasized that the new free jet spectroscopy would provide an unprecedented ability to study unusual molecular species typically found only at very high temperatures (radicals and ions found in flames and plasmas) or at extremely low temperatures (weakly bound van der Waals complexes and aggregates). Although the implementation of these ideas seemed somewhat difficult at the time, recent technological advances in the design of supersonic devices and in high resolution laser spectroscopy have brought us to a stage where much of the promise of Milne and Greene's concept of free jet isolation spectroscopy can now be fulfilled.

In the remaining portion of this Account we will describe several examples of recent applications of optical spectroscopy in supersonic beams and jets. This presentation is intended to be illustrative and is in no way expected to serve as an exhaustive review.

Of all the many spectroscopic techniques one can conceive in the optical region of the spectrum, fluorescence excitation offers a great manipulative simplicity and great sensitivity in the study of cold molecules in free supersonic jets. The simplest spectroscopy,

direct measurement of light absorption, is rather difficult to carry out with a sample as rarified and as limited in extent as a supersonic free jet or molecular beam. Recently, however, there has been an experiment where the direct absorption spectrum of a molecular species cooled in a supersonic expansion was measured successfully. Using a tunable diode infrared laser, researchers at the Los Alamos Scientific Laboratory[16] have recorded the high resolution infrared absorption spectrum of UF_6 cooled to 30K in a low Mach number expansion of helium in a convergent/divergent nozzle. The spectroscopic experiment was performed on the relatively high density gas within the divergent section of the nozzle where the expansion was constrained by the nozzle walls to attain a fixed Mach number. Although the results of this type of experiment may be quite important for possible laser induced isotope separations and laser induced chemical reactions, the limited final vacuum precludes attainment of the extremely low internal temperatures which are desirable for most spectroscopic applications. The performance of direct absorption spectroscopic experiments on supersonic free jets appears feasible but, to the authors' knowledge, no successful experiments of this type have yet been performed.

One of the earliest examples of fluorescence spectroscopy is provided by the work of Robben and Talbot[17] in 1966 where the fluorescence of the $B^2\Sigma^+$ state of N_2^+ was excited by crossing a supersonic free jet of N_2 by a well-collimated 30 keV electron beam. Analysis of the dispersed fluorescence permitted the measurement of the N_2 rotational temperature in the expanding jet. More recently, the advent of lasers – particularly tunable dye lasers – has permitted a wide range of optical experiments on free jets. Sinha et al[18] have used both white light and lasers to study the internal state distribution of K_2 and Na_2 in a supersonic beam, and to study the alignment induced in ensembles of these molecules as a result of the supersonic expansion.[19] Bergmann et al[20] have used a

single mode cw dye laser to measure the velocity and internal state distributions of Na_2 in effusive and supersonic beams.

Over the past few years at the University of Chicago we have performed a variety of laser experiments with supersonic beams and jets which begin to demonstrate a few of the many advantages of "free jet isolation spectroscopy" as envisioned by Milne and Greene. In these experiments the molecule of interest is seeded in low concentration into a rare gas, and the cooled molecules are excited with a tunable cw dye laser. The resulting fluorescence is usually detected without wavelength dispersion, and the spectrum is then a plot of the total detected fluorescence versus exciting wavelength. Since the molecule can only fluoresce if it is excited, and it can only be excited if the laser is tuned to an absorption frequency, the fluorescence excitation spectrum is very similar to the absorption spectrum. One important difference arises because some states may decay via radiationless processes. In these cases the molecule may have a well developed high resolution absorption spectrum and no fluorescence excitation spectrum. A summary of some results of the application of this technique to a variety of molecular systems is presented below.

NITROGEN DIOXIDE

So much effort has gone into the analysis of the visible spectrum of NO_2 that it has almost become a sub-branch of molecular spectroscopy. In spite of all this work, only in the last few years have even the most gross properties of the excited state been determined. There are two basic problems which have prevented analysis of the spectrum. In the first place, the spectrum is very extensive and very dense, and there are far too many lines for an easy assignment. The spectrum extends from beyond the dissociation limit near 4000Å

in the blue to at least 8000Å in the infrared and this entire region has a very high density of lines. In the second place, this forest of lines has, in most regions, no obvious periodicity or regularity and the standard methods of analysis for molecular spectra do not apply. With the development of high resolution laser-induced fluorescence spectroscopy it became possible to assign the rotational quantum numbers of any particular rovibronic line in the spectrum, [21] but only in rare instances was it possible to isolate and assign a set of lines belonging to a single vibronic band. [22] These problems are illustrated in Fig. 4a which shows a portion of the room temperature fluorescence excitation spectrum of NO_2.

When a mixture of a few percent NO_2 in argon is expanded through a supersonic nozzle, the NO_2 may be brought to a rotational temperature of a few degrees Kelvin, [23] and this cooling leads to a substantial simplification of the spectrum as shown in Fig. 4c. At these rotational temperatures only the lowest few rotational levels are populated and, most important, for the first time the individual vibronic bands are well separated. The rotational assignment of most of the bands is now a straightforward manner and this is illustrated for a typical band in Fig. 5. Thus far, a 1000Å region from 6700 to 5700Å has been examined at high resolution and, in this region, 140 vibronic bands have been identified and analyzed. [24] More recently, expansion of a dilute mixture of NO_2 in helium at 100 atm has formed a supersonic jet wherein NO_2 has been cooled to a rotational temperature of ~0.7K and a vibrational temperature of ~150K. At these temperatures more than 98% of all NO_2 molecules are in the lowest allowed quantum state. The fluorescence excitation spectrum of such a jet is quite simple: effectively only a single line (R(0)) for each vibronic cold band.

The principle result of all this work has been to document just how complicated the NO_2 problem is. It has long been known that the visible spectrum of NO_2 was highly

perturbed, and the most likely candidate for the perturbing states were high lying vibrational levels of the ground $^2A_1$ electronic state. Nonetheless, there was the hope that there were enough unperturbed levels so that if only they could be found and assigned, the structure of the excited state could be determined by the usual methods of spectral analysis. The fact that there are 140 vibronic bands of similar intensity in a 1000Å interval indicates that essentially all of the high lying levels of the ground electronic state have borrowed absorption intensity by mixing with the excited electronic state, and there is no way of distinguishing the two states in this region. This suggests that there are no unperturbed electronic states in the visible and that the molecule does not have a structure characteristic of a single electronic state, but that each vibronic level has a structure of its own which depends on the details of the mixing of electronic states. Recently, Jackels and Davidson[25] have shown that the mixing of the ground $^2A_1$ and excited $^2B_2$ states is similar to a John-Teller mixing and that the pure states of different C_{2v} symmetry are not even approximately eigenstates of the molecule. The supersonic beam data tend to support the validity of their model.

TETRAZINE

For molecules as large or larger than benzene the traditional techniques of high resolution gas phase spectroscopy begin to be inapplicable even for molecules which (unlike NO_2) have well-separated electronic states. The rotational structure in the spectra of such molecules becomes so dense that it is frequently impossible to assign individual rotational transitions. Usually, molecules of this size have a number of low frequency vibrational modes which, along with the extensive rotational structure, produce gas phase spectra which are prohibitively complex. Supersonic free jets may be expected

to alleviate this difficulty for a wide range of molecules previously considered to be far too large for gas phase spectroscopy.

For example, we have recently observed the fluorescence excitation spectrum of s-tetrazine[26] cooled in a free expansion of a dilute mixture in helium. Figure 6 shows a portion of the 0-0 band of the $^1B_{3u}(n\pi^*) \leftarrow\, ^1A_g$ transition of this molecule at high resolution in a supersonic free jet. The free expansion has cooled the tetrazine to a rotational temperature of $\sim 0.5K$ which for this molecule is sufficient to permit a straightforward and complete analysis of the rotational structure.

An interesting sidelight of this analysis is derived from measurements of the asymmetry splitting of the transitions arising from $K=1$ levels of this near symmetric oblate top. It turns out that the magnitude of this splitting and its dependence upon J can only be explained if the inertial $\underline{A}$ and $\underline{B}$ axes of the molecule are allowed to interchange as a result of the optical transition. This phenomenon, called axis interchange, was first observed in pyrazine.[27]

van der Waals Complexes

At the translational temperatures available with supersonic jets, the binding energy produced by van der Waals forces can be very much larger than KT, and in this case the complexes known as van der Waals molecules are stable and may be studied spectroscopically. A large and very interesting body of data is emerging from magnetic and electric resonance studies of these species, and only limitations of space force us to confine our attention to optical studies.[28] The same type of information as obtained by molecular beam resonance techniques for weakly bound molecular complexes may also be obtained in laser experiments on free, supersonic jets. The requirement for electric or magnetic resonance, that the complex possess a substantial dipole moment in the ground electronic state (or a metastable

excited state), is replaced in the laser experiment by a requirement that the complex have a nonvanishing electric dipole optical transition moment to an upper state having a substantial fluorescence quantum yield. These optical measurements have the additional advantage that transitions to excited vibrational states of the complex can be observed. This may permit a detailed measurement of the potential which binds the complex together and allow the study of vibrationally predissociating states. A few examples are described below.

HeNO$_2$

As described previously, when NO_2 is suspended in a helium carrier gas, the rotational cooling may be made to proceed to the point where essentially only the lowest rotational level of NO_2 is populated. When this is done a new weak feature appears in the spectrum accompanying each vibronic band as shown in Fig. 7. This feature is characterized by being substantially wider (~ 0.8 cm^{-1}) than the NO_2 spectral lines and it is attributed[29] to the van der Waals complex of helium with NO_2. As far as we know, this and the HeI$_2$ complex to be described next, are the first examples of a complex of helium bound to a molecule.

The width of the van der Waals line is due to uncertainty broadening caused by the short excited state lifetime of the complex. The observed broadening indicates the helium survives for an average of ~ 250 vibrational periods of the NO_2 bending mode before it is knocked off in the vibrational predissociation. At the excitation wavelengths used in these experiments, the NO_2 is excited to an upper state with at least several thousand wavenumbers of excess vibrational energy and the van der Waals bond is almost certainly no stronger than 100 wavenumbers. Therefore, the surprising thing is not that the line is broadened, but that the lifetime of the complex with respect to vibrational predissociation is as long

as it is. Since the lifetime of the complex is very much shorter than its radiative lifetime, the fact that we see any fluorescence indicates that the complex photodissociates into a helium atom and an electronically excited NO_2 molecule (NO_2^*), and it is the fluorescence from NO_2^* that we are observing. The fact that the complex line is never displaced by more than a few wavenumbers indicates that the van der Waals potentials must be very similar in the ground and excited electronic states.

HeI$_2$

When a small amount of I_2 is seeded into helium, the fluorescence excitation spectrum shown in Fig. 8 may be produced, and from this spectrum one may obtain quantitative information about the extent of rotational and vibrational cooling in the expansion. Under the conditions used to produce Fig. 8, the translational temperature is expected to be ~ 0.1K. If one plots the concentration of the various rotational levels as obtained from the spectrum versus the rotational energy as is done in Fig. 9, one sees that the lower levels attain a Boltzman distribution at a rotational temperature of about 0.5K while the higher levels depart somewhat from this distribution. If one calculates a vibrational temperature from the ratio of concentrations of the two observed vibrational levels of the ground electronic state using the observed intensities and the known Franck-Condon factors, one obtains a vibrational temperature of around 50K.

The spectrum of iodine has been extensively studied and there seems to be little new information in this region of the spectrum that can be added from the supersonic jet experiment. However, in addition to the iodine spectrum, one can also observe spectra of the van der Waals complexes of HeI$_2$ and He$_2$I$_2$, as shown in Fig. 10, and these can only be studied in the cooled jet. As in the case of HeNO$_2$, the complex bands are always very close to the parent I$_2$ band, and therefore once again electronic or vibrational excitation

of the molecule does not seem to change the van der Waals potential very much.

Again, one of the most interesting features of the complex spectra is the narrowness of the lines and the implied long lifetime of the excited electronic state. As shown in Fig. 11, the lines are narrow enough so that rotational structure is well resolved even through there is more than enough energy in the I_2 stretching vibration to dissociate the van der Waals bond. As the I_2 stretch is excited to higher and higher levels, the lifetime does decrease somewhat, but the lifetime is not a strong function of the excess vibrational energy and the complex is always able to live for a great many I_2 vibrational periods.

X-Tetrazine and X_2-Tetrazine (X = He, Ar, H_2)

The formation of van der Waals complexes with s-tetrazine is a particularly facile process in the supersonic jet. Even at rather moderate expansion conditions (compared to those used in the NO_2 and I_2 experiments) spectral features are observed due to the He-s-tetrazine and He_2-s-tetrazine van der Waals complexes as shown in Fig. 6. Analysis of the rotational structure shows that the complexes are fairly rigid with the helium atom located above the plane of the ring in the He-s-tetrazine and both above and below the ring in He_2-s-tetrazine. In all cases, including both electronic states (X ^1A_g and B $^1B_{3u}$) the helium atoms are on or very close to the out-of-plane C_2 symmetry axis at a distance of 3.3Å from the ring. This implies a He-C distance of 3.6Å which is very close to that predicted by Bernstein's rule of thumb (B).[31] In both complexes we have observed at least one member of a vibrational progression in one of the van der Waals bond modes, permitting a measurement of the van der Waals frequency which turns out to be ~ 38 cm^{-1} for both complexes.

These two locations in the s-tetrazine molecule (above and below the ring, in the center) appear to be particularly good van der Waals binding sites. Under the most extreme

cooling conditions attainable in the present supersonic apparatus, approximately 80% conversion is obtained of the s-tetrazine into the He_2-s-tetrazine complex. Spectral features due to a He_3-s-tetrazine complex have yet to be identified even with these high expansion conditions.

Since the 0-0 band of tetrazine and its complexes is observable, the problem of vibrational predissociation does not arise. We have, therefore, been able to observe van der Waals complexes of tetrazine with both Ar and H_2. Although we are only beginning the study of these species, the first data indicates that, as expected, the Ar and H_2 complexes are more stable than the He complex. There is also an indication that, at least in the case of the H_2 complex, the hydrogen lies above the plane of the ring in the C_2 axis.

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FIGURE CAPTIONS

Fig. 1   Velocity distribution in effusive molecular beam (dashed curve) and supersonic molecular beam (solid curve). Both curves are normalized to unity at the most probable velocity and are for helium at a reservoir temperature of 300K. The curve for the supersonic molecular beam assumes the gas has been expanded to Mach 30.

Fig. 2   Terminal Mach number versus $(P_o D)$ for a classical gas and for helium. Figure is from ref. 10.

Fig. 3   Shock structure surrounding the expanding gas of a free jet. Nozzle pressure is P_0, ambient pressure in expansion chamber is P_1, D is the diameter of the nozzle opening, X_m is the distance to the mach disk from the nozzle.

Fig. 4   A portion of the fluorescence excitation spectrum of NO_2 for (top) a conventional room temperature sample of pure NO_2 at 0.04 torr pressure, (middle) a supersonic beam of pure NO_2, and (bottom) a supersonic beam of 5% NO_2 in Ar. All spectra were taken using a cw dye laser. Laser bandwidth was 0.5Å for the lower two spectra.

Fig. 5   Fluorescence excitation spectrum of NO_2 in the region of 5932 Å showing vibronic band number 99 (see Table I in ref. 24). Downward-going frequency marks are 75 GHz apart and upward-going frequency marks are 7.5 GHz apart.

Fig. 6   The fluorescence excitation spectrum of the 0-0 band of the $^1B_{3u} (n\pi^*) - {}^1A_g$ transition in s-tetrazine showing spectra of the species tetrazine, He-tetrazine, and He_2-tetrazine.

Fig. 7   A portion of the fluorescence excitation spectrum of a 1% NO_2 in helium mixture recorded at low (a) and high (b) sensitivity. The broad features seen at high sensitivity are due to the $HeNO_2$ van der Waals molecule.

Fig. 8   High resolution spectrum of the 10-0 and 12-1 vibronic bands of the $\tilde{B} \leftarrow \tilde{X}$ transition of iodine in the supersonic jet. The fluorescence detection optics for this spectrum were adjusted to allow for a 200 MHz doppler width and the dye laser was adjusted so as to lase on a single longitudinal mode of the laser. The laser scan was accomplished by forcing the laser to hop from one longitudinal mode to the next. Mode spacing was 95 MHz.

Fig. 9   Plot of the observed intensity of members of the P branch of the 10-0 vibronic transition of I_2 in the supersonic jet ($P_0 = 91$ atm, $D = 25$ μm, $X = 0.5$ cm. The axes have been chosen so as to produce a linear plot for a Boltzmann distribution of intensities.

Fig. 10   Fluorescence excitation spectrum of a supersonic jet of I_2 in He in the spectral region near the 10-10 vibronic band of the $\tilde{B} \leftarrow \tilde{X}$ transition of I_2. Laser bandwidth was 1 GHz FWHM.
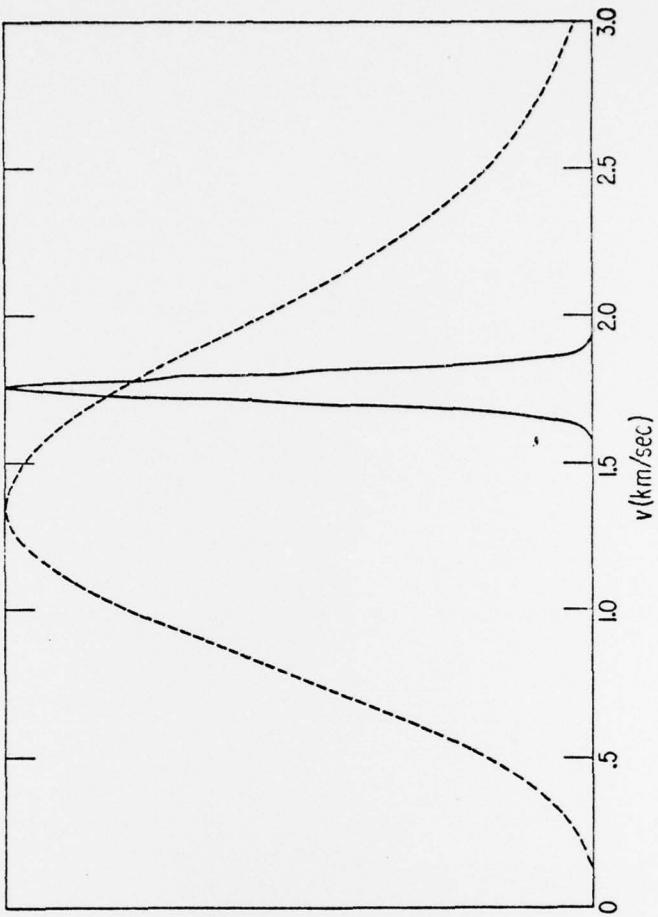
Fig. 11   Fluorescence excitation spectrum of the HeI_2 complex band corresponding to the 7-0 band of I_2. Laser and detection conditions were the same as those used to obtain the spectrum of Fig. 8. In this case, however, the laser was deliberately made to cross the free jet close into the nozzle so as to reveal a more extensive rotational structure due to the higher rotational temperature of the gas in this intermediate stage of the expansion. Labeled in the figure is X, the distance out from the nozzle to the line of laser intersection, and P_0, the nozzle pressure in atmospheres.


FIG. 1

FREE JET EXPANSION

FIG. 2

HELIUM

Terminal Mach Number vs $P_o D$ (torr-cm)

Quantum Mechanical Gas

Classical Gas

JET BOUNDARY

REFLECTED SHOCK

MACH DISK (SHOCK)

ISENTROPIC CORE

BARREL SHOCK

$$\frac{x_m}{D} = .67 \left[\frac{P_o}{P}\right]^{\frac{1}{2}}$$

FIG. 3

FIG. 5

Plot showing PHOTONS / SEC. ($\times 10^6$) versus EXCITATION FREQUENCY (GHz), with $V_0 = 16,851.2$ cm^{-1}. Frequency axis marked V_0-150, V_0, V_0+150, V_0+300; intensity axis from 0 to 0.7.

FIG. 4

Spectra at 300 °K, 30 °K, and 3 °K plotted versus WAVELENGTH (Å), from 5800 to 6100.

1% NO₂ IN HELIUM

P₀ = 104 ATM
D = 25 μ
X = 0.33 cm

(a)

(b)

FREQUENCY (cm⁻¹)

FIG. 7

FIG. 6

FIG. 9

ROTATIONAL TEMPERATURE

0.4 K

$J(J+1)$

ln (INTENSITY / J)

FIG. 8

0.3 ppm IODINE IN HELIUM

P_2 = 91 atm

D = 25 μ

V_0 = 16,894.7 cm^{-1}

10-0 BAND

12-1 BAND
(INTENSITY × 3.3)

FREQUENCY (GHz)

PHOTONS / SECOND (× 10^5)

He I$_2$

(7-0) BAND

X = 0.15 cm
P$_0$ = 98 atm

X = 0.05 cm
P$_0$ = 70 atm

PHOTONS / SEC. (x 10^4)

2.4 1.8 1.2 0.6 0

4 3 2 1 0

14 ·4 -14 -28 -42 -66 -80 -94 -108

FREQUENCY (GHz)

FIG. 11

0.3 ppm IODINE IN HELIUM

P$_0$ = 84 atm

D = 25 u

V$_0$ = 16,895.0 cm

I$_2$ 10-0 BAND

I$_2$ 12-1 BAND

I$_2$-He 10-0 BAND

I$_2$-He$_2$ 10-0 BAND

PHOTONS / SECOND (x 10^4)

5 4 3 2 1 0

-420 -210 V$_0$ 210 420 630

FREQUENCY (GHz)

FIG. 10

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This account is a description of a recent technique which is directed toward overcoming two difficulties which arise when one wishes to study the high resolution spectra of molecules. The first of these is the necessity of obtaining a sample of the molecules at a temperature which is low enough to prevent thermal dissociation and which contains population of only as many rotational and vibrational levels of the molecular system as can be separately assigned in the spectrum. The second difficulty lies in finding a medium which will support

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20. Abstract (cont'd)

the molecular system at this low temperature without introducing undesirable changes and complications in the spectrum. A desirable spectroscopic sample would be an ensemble of molecules, all in a particular and well-defined quantum state (usually the lowest energy allowed state) traveling in free space with a narrow velocity distribution, and at a sufficiently low density so that intermolecular interactions are unimportant.

A supersonic expansion of molecules in an inert, monatomic carrier gas seems, to a large degree, to satisfy the requirements of an ideal spectroscopic sample. In the course of such a supersonic expansion, the translational temperature of the carrier gas falls to an extremely low value – less than 0.03K in some cases. Polyatomic molecules seeded into this expanding gas communicate with the low temperature bath provided by the monatomic carrier via two-body collisions, causing the translational and rotational degrees of freedom of the molecules to cool to comparable low temperatures. Vibrational cooling, although less complete than rotational cooling, can also be quite extensive. The rapidly falling temperature and density in the resultant supersonic jet quickly brings the expanding gas into a condition of free, collisionless flow, permitting molecular species which would otherwise be highly unstable to survive, unperturbed, at a very low temperature for a period of time limited only by the size of the apparatus. Because this cooling occurs so quickly, in a manner which minimizes three-body collisions, the cooling may be achieved without extensive condensation.

The purpose of this account is to trace the progress of research in the application of supersonic beams and jets toward the solution of a number of problems in molecular optical spectroscopy and to illustrate the promise such experiments hold for future work.